The Analysis of Glycerol by Gas Chromatography

JAMES SNYDER and **BORIVOJ FRANKO-FILIPASIC**, Agricultural Chemical Division, FMC Corp., PO Box 8, Princeton, NJ 08540

ABSTRACT

Commerical glycerol and its organic impurities can be measured accurately by a single gas chromatographic GC analysis utilizing Tenax-GC® and flame detection.

INTRODUCTION

Glycerol is analyzed industrially either by determining the apparent specific gravity of the glycerol-water mixture (AOCS Official Method Ea 7-50) or by oxidation of glyerol with sodium periodate to formic acid which is titrated with a suitable base (AOCS Official Method Ea 6-51). The specific gravity is an extremely precise and rapid physical method for the pure mixture; the effect of various common impurities on the gravity has not been determined. It has the additional advantage of a simultaneous water analysis. The periodate method is the only method of chemical analysis for glycerol; it is subject to error from other polyglycols and is not as simple and rapid as the measurement of specific gravity by a pycnometer. Other impurities generally common to natural glycerol are identified by a variety of wet methods summarized in the standard methods of analysis(1). The present state of glycerol analysis is well summarized by Ashworth(2).

Our initial efforts to develop a direct method utilizing gas chromatography (GC) failed due to poor separation by the available packings and pyrolysis in the column caused by the high temperature required to elute the products. The most successful was a silylation procedure which only failed where extensive impurities were present which either did not silylate or gave too many overlapping peaks due to similar polyhydroxy impurities.

The analytical scheme here presented is a rapid and reliable method for the assay of glycerol and organic impurities. This reliability allows routine analysis while obviating the necessity of further tests for organic impurities which affect the accuracy of other methods. Glycerol and its impurities are assayed by GC while the water is assayed by the Karl Fischer Method (AOCS Ea 8-58). Although water can be determined by GC, it cannot be used in this method, as many process streams are aqueous and neat glycerol itself must be diluted with water to allow for proper injection.

EXPERIMENTAL

This method for the analysis of glycerol used Tenax-GC® column packing (distributed by Applied Science). The success of this method is due to the stability of the packing at

TABLE I

Retention time (min)	Molecular weight	Name	Structure
4.31	74	β-Hydroxypropionaldehyde	$HOCH_2-CH_2-CHO$
5.8	90	1,2-Butanediol	H_2C—CH-CH_2-CH_3 OH OH
8.7	92	Glycerol	H_2C—CH—CH_2 OH OH OH
10.5	134	1-Monacetin	H_2C—CH—CH_2 OH OH $OCOCH_3$
12.2	148	Acetol glycerol ketal	H_2C—CH—CH_2OH O O \ / HOH_2C-C—CH_3
14.9	148	β-Hydroxypropionaldehyde glycerol acetal	H_2C—CH—CH_2OH O O \ / CH-CH_2-CH_2OH
15.6	148	*trans*-2,5-*bis* (hydroxymethyl) 1,4-dioxane	O CH_2OH HOH_2C O
17.2	148	*cis*-2,6-*bis* (hydroxymethyl) 1,4-dioxane	O HOH_2C CH_2OH O

the high temperatures needed for the separation of glycerol and its impurities without catalyzing sample decomposition.

The equipment consisted of a HP 5840 chromatograph equipped with flame ionization detector, magnetic card reader, and an autosampler; and a 3m (10 ft) long, 6mm/2mm diameter glass column, packed with 250/180 µm (60/80 mesh) Tenax-GC®, with glass-lined injection ports.

The use of glass columns allows for ease of packing and elimination of metal contamination which contributes to decomposition of the sample. The glass-lined injection ports prevent packing contamination by removing salts that are present in certain samples: the nonvolatile salt contaminates only the readily replaced glass liner rather than the column packing. The use of an autosampler increases the precision over hand injection. As water is not detected by flame ionization, pure glycerol samples are diluted to ~50/50% with water to overcome the viscosity problem; many process streams do not need dilution.

The conditions were: column: Tenax-GC®, program: 150-240C at 10 C/min, 15 min hold at 240 C, injection t: 240 C, flame detector t: 240 C, carrier: He 45 mL/min, chart speed: 0.5 in min, sample: glycerol 1 µL (~ 50/50 H_2O).

The instrument's operating parameters are optimized for glycerol and are periodically checked by running a standard at random intervals of 20-40 samples – the standard is any reagent grade 99.5% glycerol. Replicability of the glycerol peak is within 0.02 area %.

RESULTS AND DISCUSSION

Once the chromatographic separation technique was proven reliable, samples of typical plant process and product streams(3,4) were analyzed. A number of organic compounds were separated and catalogued according to their retention time on a 10' Tenax-GC® column. Mass spectroscopy (MS) and nuclear magnetic resonance (NMR) were used to identify the separated GC peaks. These retention times and structures are displayed in Table I.

All of the compounds listed were confirmed by synthesis and injected into the column to make certain that they did not break down or rearrange. Most interesting are the two dioxanes which are formed by glycerol dehydration in the final purification columns and are excellent criteria for optimizing column operation. Although the other two dioxane isomers, *cis*-2,5- and *trans*-2,6-*bis* (hydroxymethyl) 1,4-dioxane, were not synthesized, it is assumed that they would have the same retention times at 15.6 and 17.2 min, respectively. The front and tail of the glycerol peak were examined by MS and no additional compounds were found under it.

The accuracy of the glycerol analysis was measured by comparison of GC vs periodate analyses which indicate a high correlation between the two, with GC generally indicating a slightly higher assay by ca. 0.1%. Statistical analysis of 21 sets of data showed an average difference of 0.09% (range -0.59 to +0.48%) which is not statistically different from 0.00%. Reanalysis of the same sample 30 times showed an average difference of 0.06%.

A number of samples were analyzed for monacetin concentration by caustic titration(5) and then compared with gas chromatographic analyses. The two analytical methods showed excellent agreement and statistical analysis of 79 sets of data showed an average difference of -0.04% (range -0.28 to +0.33%) which is not statistically different from 0.00%.

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